

2. (twice amended) A cocoa oil, extracted from cocoa hulls, which oil comprises free and bound phytosterols and tocals, wherein the free phytosterols comprise campesterol, β -sitosterol, stigmasterol, cycloartenol, and 24-methylene cycloartenol and wherein the tocals comprise tocopherols and tocotrienols.

REMARKS

Claims 2, 5-11, 15-18, 20-23, and 29 are presented for examination. Claims 3, 4, 19, and 29 are canceled. Claims 1, 12-14, and 24-28 are restricted out.

A. Amendment

Support for amended Claim 2 can be found in canceled Claims 3, 4, and 29.

B. §112 Rejection

Claim 19 is rejected as indefinite because the Examiner considers the phrase "fractionating the cocoa oil by . . . chromatography" to be steps that would not purify the oil. He believes they are analytical steps to assay the various components in the oil. He cites to pages 9-12 of the specification. He considers the fractionation – chromatographic steps of Claim 19 to be outside the scope of Claim 15 which is directed to a process for extracting cocoa oil comprising phytosterols and tocals from cocoa hulls and not to a process for obtaining various fractions/constituents therefrom. Again the Examiner strongly suggests that Claim 19 be canceled.

C. Applicants' Response To § 112 Rejection

It is respectfully submitted that the purification of phytosterols is supported by the disclosure at page 4, 6th full paragraph, where it is taught that "The phytosterols may be purified by preparative high pressure liquid chromatography or column chromatography." (emphasis added). The pages relied upon by the Examiner, *i.e.*, pages 7-9, teach the fractionation of the oil

which also purifies the oil. The literature supports Applicants' position that preparative high pressure liquid chromatography and column chromatography can be used to separate (*i.e.*, fractionate) and/or purify phytosterols and tocopherols.

See U.S. 6,395,915 at column 1, lines 59 where it is taught in the "Description of Prior Art" that "Prior art liquid chromatography methods ... can thus be broken into two categories: analytical liquid chromatography methods designed to resolve the different components at very low levels to permit analysis with bench top analytical HPLC equipment; and preparative (process) liquid chromatography methods designed for the commercial purification of specific components out of a crude feedstock." The '915 patent claims are directed to a method of isolating tocotrienols, tocopherols and isomers thereof from a crude initial stock using reverse phase liquid chromatography (see Claim 1).

See U.S. 4,882,065 which discloses the separation and purification of sterols from a feed mixture comprising the sterols and impurities including terpene alcohols, fatty alcohols, diterpene aldehydes and polymeric materials. The mixture is contacted with an adsorbent and the adsorbed sterols are then desorbed by passing a suitable solvent through the adsorbent. The adsorbent (*e.g.*, activated carbon) is contained in a column having at least 3 serially interconnected zones, the 1st zone being an adsorption zone, the 2nd zone being a purification zone, and the 3rd zone being a desorption zone.

Thus, the claimed phytosterols and tocopherols can be purified by preparative high pressure liquid chromatography and column chromatography. However, if the rejection is maintained and the other claims are allowed, Applicants will cancel Claim 19. Reconsideration of its rejection is respectfully requested.

D. §102(b) Rejection Over El-Saied et al.

Claims 2-6, 9-11, and 29 are rejected under §102(b) as being anticipated by El-Saied et al. (Zeitschrift Fuer Erna., 1981).

According to the Examiner, El-Saied et al. teach a fat which contains phytosterols such as those claimed and which is obtained from cocoa shells (hulls) by hexane extraction followed by evaporation of the hexane. The Examiner explains that the reported chromatographic analyses shows that cocoa shell fat is similar in composition to cocoa butter (citing pages 145-146, Materials and Methods and pages 149-150 under the heading *Unsaponifiable matter composition*). The Examiner states that, based upon the teachings in the specification, c.g., Claim 16, the cocoa shell fat of the reference, obtained by hexane extraction would inherently comprise tocots such as the claimed tocopherol and tocotrienol since hexane is disclosed and claimed as a suitable solvent for extracting both the claimed phytosterols and claimed tocots and for producing the claimed cocoa oil.

The Examiner believes "fat" reads upon "oil" because oil is naturally present in fat and, thus, fat is inherently comprised of oil. He points out that "fat" is defined as "a solidified animal or plant oil", citing Webster's II New Riverside University Dictionary, 1988. Therefore, the Examiner concludes that the reference anticipates the rejected claims.

E. Applicant's Response to §102(b) Rejection Over El-Saied et al.

It is respectfully submitted that the fact that "fat" is a "solidified oil" does not mean they are identical. If their compositions were the same, their physical state at room temperature would be the same.

It is recognized that the composition of fats and oils is very complex. See Table 17.3 from the Morrison and Boyd book, "Organic Chemistry". See also "§17.27 Unsaturated fats.

Hardening of oils. Drying Oils” where it is explained that “. . . unsaturation in a fat tends to lower its melting point and thus tends to make it a liquid at room temperature.” It is further explained that “Hydrogenation not only changes the physical properties of a fat, but also —and this is even more important — changes the chemical properties: a hydrogenated fat becomes *rancid* much less readily than does a non-hydrogenated fat.” (emphasis in original). See pages 493-499 from the Morrison and Boyd book attached as Exhibit 1.

The El-Saied et al. article does not support the Examiner’s position that cocoa shell fat and cocoa butter are similar. It confirms Applicants’ position that they are different. These two fats, (i.e., cocoa butter from the roasted cocoa nibs and cocoa shell fat from roasted cocoa husks’) have different physical and chemical constants (see Table 1), different lipid classes (see p. 148), different fatty acid compositions (see Table 4), and different sterol compositions (see Table 5) even though they are from the same cocoa beans. Please note that under “materials” it is taught that “[s]amples of cocoa butter and cocoa shell from the same cocoa beans were obtained from the Egyptian Company for Foods (Bisco-Mars Chocolate Factory, at Alexandria, Egypt” (emphasis added).

If these two fats from the very same cocoa beans are different, it is reasonable to conclude that Applicants’ cocoa oil and El-Saied’s cocoa shell fat are not going to have the same composition. Please note that Applicants’ cocoa oil has a total sterol content of 4,674 compared to 205 for cocoa butter (which the Examiner equates with cocoa shell fat) (see Table 1 on page 10). Also note that there were 4396 mg of unsaponified sterols and 4,674 mg. of saponified sterols per 100 gm of roasted cocoa hull oil compared with 86 mg of unsaponified sterols and 205 mg of saponified sterols in cocoa butter. The percentage of “free sterols” in the roasted cocoa hull oil was 94% compared to 42% for cocoa butter (see Table 3 on page 12).

F. §102(b) Rejection Over Baskakova et al. or Gavrilenko

Claims 2-11 and 29 are rejected under §102(b) as being anticipated by Baskakova et al. (SU 1734748 – DWPI Abstract) or by Gavrilenko (Maslo-Zhir. Prom-st., 1977-CAPLUS Abstract).

According to the Examiner, Baskakova et al. teach a cocoa husk (hull) oil which would inherently contain the claimed phytosterols and tocopherols since these are natural constituents of cocoa husk (hull) oil. According to the Examiner, Gavrilenko teaches a solvent-free oil extracted from cocoa husks (hulls). The Examiner believes that the crude and refined cocoa husk oil taught by Gavrilenko would inherently contain the claimed phytosterols and claimed tocopherols since these are natural constituents of cocoa husk (hull) oil.

The Examiner points out that the patentability of a product does not depend on its method of production.

G. Applicant's Response to §102(b) Rejections Over Baskakova et al. and Gavrilenko

Applicant respectfully submits that the Baskakova et al. English abstract is not enabling. It does not teach one skilled in the art how to make the cocoa husk oil used in the lipstick composition. To be prior art under §102(b), the reference must put the anticipating subject matter at issue into the possession of the public through an enabling disclosure. *Chester v. Miller*, 906 F. 2d 1574, 15 USPQ 2d 1333 (Fed. Cir. 1990).

The Gavrilenko English abstract is also not enabled. It does not teach one skilled in the art how to extract the oil "from cocoa husks (containing 5-10% crude oil)". Rather, it teaches one how to refine the extracted oil by washing, neutralizing, rewashing, drying, and deodorizing.

The Abstracts are silent regarding the presence of phytosterols and/or tocopherols in the cocoa oils. As the Examiner is aware "[I]nvalidity by anticipation requires that the four corners of a

single, prior art document describe every element of the claimed invention, either expressly or inherently, such that a person of ordinary skill in the art could practice the invention without undue experimentation. *Advanced Display Systems, Inc. v. Kent State University*, 212 F3d, 1272, 54 U.S.P.Q. 1673 (Fed. Cir. 2000). It is respectfully submitted the Abstracts the Examiner relies on do not anticipate the claimed cocoa extract comprising "free" and "bound" sterols and tocopherols. The Abstracts do not anticipate cocoa oils comprising "campesterol, β -sitosterol, stigmasterol, cycloartenol, and 24-methylene cycloartenol". The Examiner has cited no reference supporting his position that phytosterols and tocopherols are inherently present in cocoa husks.

If requested, Applicants will provide the full texts of the Basokova et al. Russian patent and Gavrilenko Russian article for the Examiner's convenience in determining how the cocoa oils were prepared.

Applicants recognize that the patentability of the claimed cocoa oil does not depend on its method of preparation; however, without more information about the prior art cocoa oils it is impossible for Applicants to distinguish their cocoa oil from these prior art cocoa oils.

H. §102(b)/103(a) Rejection Over Warocquier-Clerout et al.

Claims 2-11 and 29 are rejected under §102(b) as anticipated by or, in the alternative, under §103(a) as obvious over Warocquier-Clerout et al. (Int. J. Cosmetic Sc., 1992). According to the Examiner, Warocquier-Clerout et al. teach a lipid extract (which the Examiner believes reads upon an oil extract) termed ICSB of cocoa shell butter which is extracted therefrom. The starting cocoa shell butter is obtained from cocoa shells using solvents including petroleum spirits (which are synonymous with petroleum ether). Based upon subsequent fractionation thereof using silica gel column chromatography, the ICSB lipid/oil extract was shown by Warocquier-Clerout et al. to contain various phytosterols (such as those claimed and disclosed)

as well as tocots (such as those claimed and disclosed) – see, e.g., page 39, *Synopsis*; page 40, second full paragraph; and pages 41-42 in the Result section under the heading *Preparation and Fractionation of ICSB* including Table 1 and Figure 1). Accordingly, the Examiner concludes that the cited reference discloses a cocoa shell oil which appears to be identical to the presently claimed cocoa shell oil since it was obtained using similar extraction solvent(s) and it was shown to contain the claimed compounds.

In the alternative, even if the claimed cocoa shell oil is not identical to the reference's cocoa shell oil with regard to some unidentified characteristics, the differences between that which is disclosed and that which is claimed are considered to be so slight that the cocoa shell oil of the reference is likely to inherently possess the same characteristics as the claimed cocoa shell oil, particularly in view of the similar characteristics which they have been shown to share. The Examiner concludes the claimed cocoa oil would have been obvious to those of ordinary skill in the art within the meaning of §103. Accordingly, the claimed invention as a whole was at least *prima facie* obvious, if not anticipated by the reference, especially in the absence of clear and convincing evidence to the contrary.

1. Applicants' Response to §102(b)/103(a) Rejection Over Warocquier-Clerout et al.

It is Applicants' position that the cocoa shell butter of the reference does not anticipate or render obvious the claimed cocoa oil for the reasons discussed above in Section D. Cocoa shell fat and cocoa oil are not the same.

This reference does not disclose how the cocoa shell fat was obtained and its disclosure is not relevant because it relates only to the preparation of a non-saponifiable lipid fraction of cocoa shell butter. It is that fraction that was eventually extracted with petroleum spirits by

Warocquier-Clerout et al. See the discussion at page 40 regarding Extraction and Fractionation which reads:

Duplicate 5g samples were refluxed with 60 ml alcoholic potassium hydroxide for 1 h; 50 ml of distilled water was added and the non-saponifiables extracted with five 10 ml and two 50 ml portions of petroleum spirit. The combined petroleum spirit extracts were washed with three 50 ml portions of ethanol and distilled water (50/50/v/v) until neutral, evaporated over a boiling water bath and dried at 100-105° C for 30 mins. (emphasis added).

Clearly, the cocoa extract of the reference was not prepared by extracting crushed cocoa husks with petroleum ether. The fact that the subfractions contained tocopherols and sterols does not mean the extract anticipates the claimed cocoa oil which contains a mixture of free sterols and bound sterols. The extract of the reference contains only bound (i.e., non-saponifiable) sterols. Therefore, this reference can not anticipate or render obvious the claimed cocoa oils which comprise free sterols and bound sterols.

J. §103(a) Rejection Over El-Saied et al. and Warcoquier-Clerout et al. In view of Mueller and Alander and Further In View of Newton

Claims 2-11, 15-23, and 29 are rejected under §103(a) as obvious over El-Saied et al. (Zeitschrift Fuer Erna., 1981) and Warocquier-Clerout et al. (Int. J. Cosmetic Sci., 1992) in view of Mueller (J. Dairy Sci., 1959) and Alander et al. (WP 99/63031) and further in view of Newton (EP 0861600).

The Examiner points out that a method of extracting a cocoa oil from cocoa hulls is claimed, which the method comprises grinding the cocoa hulls, treating the ground cocoa hulls with a solvent which extracts phytosterols and tocopherols, removing the solvent, and recovering the oil. The Examiner notes that the primary references do not expressly teach grinding the cocoa hulls prior to extraction nor using some of the claimed extraction solvents which are taught in the secondary references. He relies on Mueller for grinding the cocoa shells prior to solvent

extraction (citing page 754) and points out that grinding of herbal parts (including nuts and seeds) prior to extraction is notoriously well known to facilitate the release of desired components during solvent extraction by maximizing surface exposure. He relies on Alander et al. for their teaching that oils extracted from various herbals, such as cocoa butter, contain phytosterols, tocopherols, and tocotrienols which can be effectively extracted using suitable extraction solvents including nonpolar solvents such as hexane and petroleum ether. He cites page 1, 3rd paragraph, pages 7-8, and page 10, 3rd full paragraph.

The Examiner believes it would have been obvious to one of ordinary skill at the time the claimed invention was made to modify the extraction procedures taught by the primary references by grinding the cocoa shells prior to solvent extraction, based upon the teachings of Mueller, and to use and/or substitute other suitable extraction solvents such as petroleum ether vs. hexane, based upon the teachings of Alander et al. with respect to their equivalency as extraction solvents for cocoa butter which El-Saied et al. teach is very similar to cocoa shell fat. The Examiner concludes that the skilled artisan would have a reasonable expectation of success in extracting cocoa shells using equivalent solvents to obtain phytosterols as well as tocopherols.

The Examiner also believes it would have been obvious to the skilled artisan to utilize micronized cocoa hulls as a starting material because Newton discloses that micronizing is a common means of breaking the outer husks/hulls of cocoa beans during processing making them a readily available source. He cites col. 5, lines 46-52. The Examiner points out the adjustment of particular conventional working conditions, e.g., removing the solvent by vacuum distillation, further exposing such an oil to chromatographic techniques, and using hulls from particular types of cocoa bean and/or from roasted or unroasted cocoa beans, is merely a matter of judicious selection and routine optimization which is well within the purview of the skilled artisan. Thus,

the Examiner concludes that the invention as a whole is *prima facie* obvious over the references, especially in the absence of evidence to the contrary.

K. Applicants' Response to §103(a) Rejection Over El-Saied or Warocquier-Clerout et al. In View of Mueller and Alander and Further In View of Newton

It is respectfully submitted that the deficiencies of the primary references are not cured by the teachings of the secondary references. The primary references teach cocoa shell fat, not cocoa oil. As was discussed above, cocoa fat and cocoa oil can not have the same composition. As shown by El Saied et al. "cocoa shell fat" and "cocoa butter", even when obtained from the same cocoa beans, have different compositions. As Applicants have shown cocoa oil and cocoa butter differ markedly in the levels of unsaponified sterols and saponified sterols, (see Table 3).

It is respectfully submitted that Applicant's prior response addressed the teachings of the references as a whole and, in addition, pointed out the deficiencies of the secondary references. Mueller does not teach grinding prior to extraction. Rather, it teaches at page 756 that "[f]inely pulverized cacao shell depleted of fat by petroleum ether extraction was added to butter oil". In the tests reported on p. 757 "... cocoa shell, cocoa extract and various extracts of these products were added to butter oil". With respect to Alander et al. the solvents are irrelevant because the lipid samples which were extracted (cocoa butter, not cocoa oil) was extracted "after alkaline hydrolysis". In other words, they extracted the unsaponifiable part of the cocoa butter, not the cocoa husks. The relevance of Newton's teaching is questionable. The use of a micronizer to dry wetted grain or seed and gelatinize the starch present in the grain or seed does not render obvious pretreating cocoa beans by micronizing to loosen the cocoa hulls.

L. Closing

Entry of this Amendment and reconsideration of the §102(b), §102(b)/§103; and §103 rejections is respectfully requested.

A marked up version showing the changes to the specification and claims is attached.

Respectfully submitted,

Date:

May 5, 2003

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MARKED UP VERSION SHOWING CHANGES**In the Specification:**

Page 4, 5th paragraph rewrite as follows:

The preferred solvents are petroleum ether, hexane, pentane, and ethyl ether. The solvent is [bc] recovered by vacuum distillation or other conventional methods.

Page 5, 3rd full paragraph rewrite as follows:

Cocoa seeds with pulp removed from *Theobroma* cocoa pods [and] were freeze-dried on a Labconco (Kansas City, MO) Freeze Dry System. The pulp and hulls were manually removed, and the freeze-dried hulls were ground to a fine powder with a Tekmar Mill (Cincinnati, OH). The ground mass was subjected to overnight extraction with redistilled petroleum ether (b. p. 38-39.6°C) in a Soxtec apparatus (Fisher Scientific, Springfield, NJ). The solvent was carefully removed by slow evaporation under a stream of nitrogen, and the resultant extracts were stored at -40°C.

Page 6, 2nd full paragraph, rewrite as follows:

Gas chromatography of sterol-TMS ether derivatives. Sterol-TMS ether derivatives were separated on a 25 m X 0.25 mm i.d. Quadrex (New Haven, CT) 50% methylphenylsilicone fused-silica capillary column, programmed at 250°C for 37 min., then 10°C/min to 300°C for 5 min on a Hewlett-Packard Model 5890A gas chromatograph. The injector and flame-ionization detector temperatures were set at 250 and 300°C, respectively. Helium was used as the carrier gas at a linear velocity (μ) of 25 cm/s. One μ L injections were split 50:1. Quantitation was achieved by the ISTD technique (11). Peak identifications were made by comparison to the retention time (t_R) [if] of authentic sterol-TMS ether derivatives and by mass spectral analysis.

Page 7, 4th full paragraph rewrite as follows:

Combined capillary gas chromatography (GC) and gas chromatography [(GC/MS)] 1 mass spectra (GC/MS) analysis were used to examine the sterol composition of the extracted cocoa oils. As shown in Figure 1, a typical sterol separation was encountered as well as the presence of several unknowns.

In The Claims

Please cancel Claims 3, 4, 19, and 29 and amend Claim 2 so it reads as follows:

2. (twice amended) A cocoa oil, extracted from cocoa hulls, which oil comprises free and bound phytosterols and tocots, wherein the free phytosterols comprise campesterol, β -sitosterol, stigmasterol, cycloartenol, and 24-methylene cycloartenol and wherein the tocots comprise tocopherols and tocotrienols.

ORGANIC CHEMISTRY

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over copper chromite.

FATS

17.23 Occurrence and composition of fats

In terms of our everyday living, by far the most important esters are those occurring naturally in animal and vegetable fats. (Liquid fats are often referred to as oils.) Such materials as corn oil, coconut oil, cottonseed oil, palm oil, tallow, bacon grease, and butter are made up largely of esters of carboxylic acids. These esters are derived from a single alcohol, *glycerol*, $\text{HOCH}_2\text{CHOHCH}_2\text{OH}$, and hence are known as *glycerides*.

With very few exceptions, the carboxylic acids from which fats are derived are all straight-chain compounds, ranging in size from three to eighteen carbons; except for the C_2 and C_4 compounds, only acids containing an even number of carbon atoms are present in any substantial amounts. Besides saturated acids, there are unsaturated acids containing one or more double bonds per molecule.

We see in Table 17.3 that each fat is made up of glycerides derived from many different carboxylic acids. The proportions of the various acids vary from fat to fat; each fat has its characteristic composition, which does not differ widely from sample to sample.

Fats make up one of the three major classes of foods (the others being carbohydrates, Chapter 30, and proteins, Chapter 33); they are used in enormous amounts as raw materials for many industrial processes. The specialized chemistry of fats is vast and complicated, particularly the biochemistry and technology. In the following sections we shall examine a tiny fraction of the chemistry of fats so that we may see the application of the fundamental chemistry of esters to these more complicated compounds.

17.24 Hydrolysis of fats. Saponification. Soap

The making of soap is one of the oldest of chemical syntheses. (It is not nearly so old, of course, as the production of ethyl alcohol; man's desire for cleanliness is much newer than his desire for intoxication.) When the German tribesmen of Caesar's time boiled goat tallow with potash leached from the ashes of wood fires, they were carrying out the same

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DERIVATIVES OF CARBOXYLIC ACIDS

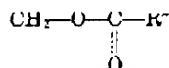
[Ch. 17]

TABLE 17.3
FATTY ACID COMPOSITION OF FATS AND OILS

Fat or oil	Saturated Acids						Unsaturated acids					
	C ₄	C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	< C ₁₈	C ₁₈	> C ₁₈	Enolic	Dienoic	Trienoic
allow	1-2 ^a	2-3	0.2	2-3	25-30	21-26	0.4-1	0.5	2-3	39-42	0.3	2
it	6-9	4-10	1-4	8-13	25-32	8-13	0.4-2	1-2	2-6	22-20	0.2-1.5	3
seed			44-51	13-18	7-10	1-4				5-8	0-1	1-3
				0-2	8-10	1-4			1-2	30-50	0-2	34-56
				0-3	17-23	1-3				23-44	0-1	34-55
				1	28-30	12-16		0.2	2-5	41-51	2-3	3-8
cornel	2-4	3-7	0-1	0-2	7-20	1-3	0-1		1-3	53-88	0-3	4-23
				1-6	32-47	1-6			0-1	10-18		2-11
				0.6	6-11	3-6	1-2		1-2	39-66		1-2
				0.3	7-11	2-5	1-3		0-1	22-34		17-33
er				2-6	7-14	0-1		0-2	10-20	25-31	C ₂₀ > C ₂₄	50-60 2-10
				0.2	5-9	4-7	0.5-1			9-29	25-32 10-20	8-29 46-67
										4-13		8-16 b

^a4% C₄, 1-2% C₁₄.

^b1-82% stearic acid, *cis*/*trans*/*trans*-9,11,13-octadecatrienoic acid, and 3-6% saturated acids.



A glyceride
(A fat)

Glycerol

Soap

Ordinary soap today is simply a mixture of sodium salts of long-chain fatty acids. It is a mixture because the fat from which it is made is a mixture, and for washing our hands or our clothes a mixture is just as good as a single pure salt. Soap may vary in composition and method of processing: if made from olive oil it is *Castile soap*; alcohol can be added to make it transparent; air can be beaten in to make it float; perfumes, dyes, and germicides can be added; if a potassium salt (instead of a sodium salt) it is *soft soap*. Chemically, however, soap remains pretty much the same, and does its job in the same way.

The cleansing action of a soap is an extremely complicated matter, but we can get some idea of the factors involved from the following simplified picture. A soap molecule has a polar end, $-\text{COO}^- \text{Na}^+$, and a non-polar end, the long carbon chain of 12 to 18 carbons; the polar end is water-soluble, the non-polar end is oil-soluble. Ordinarily oil droplets in contact with water tend to coalesce so that there is an oil layer and a water layer; but the presence of soap changes this. The non-polar ends of soap molecules dissolve in the oil droplet, leaving the carboxylate ends

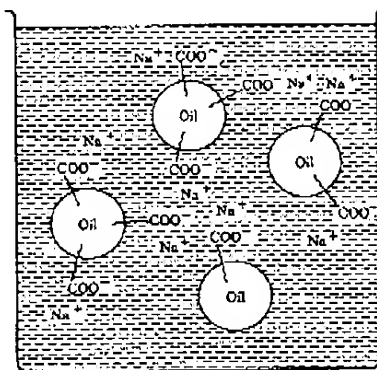


FIGURE 17.1 Emulsification of oil in water by soap. Non-polar hydrocarbon chains dissolve in oil; polar $-\text{COO}^-$ groups dissolve in water. Similarly charged droplets repel each other.

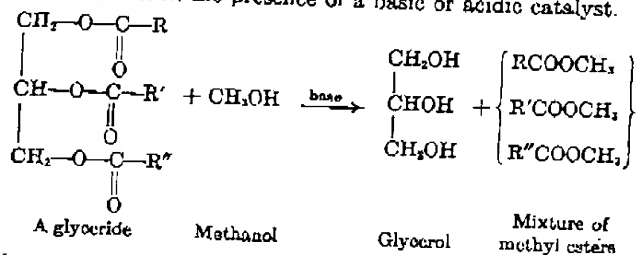
projecting into the surrounding water layer (Figure 17.1). Due to the presence of the negatively charged carboxylate groups, each oil droplet is surrounded by an ionic atmosphere. Repulsion between similar charge keeps the oil droplets from coalescing, and a stable emulsion of oil in water is thus obtained. Soap cleans by emulsifying the fat and grease that make up and contain the dirt. As we shall see, this emulsifying, and hence cleansing, property is not limited to carboxylic salts, but is possessed by any molecule containing a large non-polar portion and a polar portion (Sec. 17.20).

Hard water contains calcium and magnesium salts, which react with soap to form insoluble calcium and magnesium carboxylates (the "ring" in the bathtub).

17.25 Fats as sources of pure acids

Treatment of the sodium soaps with mineral acid (or hydrolysis of fats under acidic conditions) liberates a mixture of the free carboxylic acids. In recent years, fractional distillation of these mixtures has been developed on a commercial scale to furnish individual carboxylic acids of over 90% purity.

Alternatively, fats are sometimes converted by transesterification into the methyl esters of the carboxylic acids; the glycerides are allowed to react with methanol in the presence of a basic or acidic catalyst.



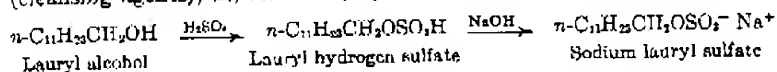
The mixture of methyl esters can be separated by fractional distillation into individual esters, which can then be hydrolyzed to individual carboxylic acids of high purity.

Fats are thus the source of straight-chain acids of even carbon number ranging from six to eighteen carbons; these in turn can be converted into alcohols by reduction (generally via their esters), and from these can be derived a host of compounds (see in Part II).

A. glyceride

The Bouveault-Blanc reduction with sodium metal and alcohol was used on a large scale during World War II when shortages of materials for the catalyst and for high-pressure equipment prevented use of catalytic hydrogenation. Since the war, chemical reduction has continued to expand and is now one of the major uses of sodium metal in this country.

The fat most commonly reduced is coconut oil, which yields a mixture containing a high proportion of the C_{12} alcohol, lauryl alcohol. Most of the alcohols obtained from fats are used in the synthesis of detergents (cleansing agents), as, for example, the salts of alkyl hydrogen sulfates:

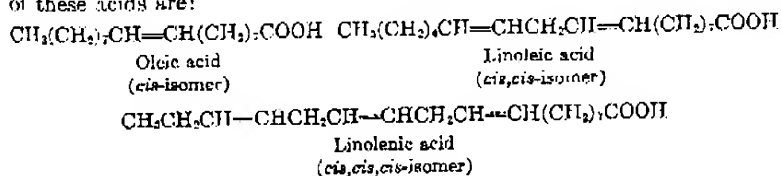


(Alkyl hydrogen sulfates are esters of sulfuric acid.) Although the synthetic detergents vary considerably in their chemical structure, the molecules of all of them have one common feature: a large non-polar hydrocarbon end that is oil-soluble, and a polar end that is water-soluble. In the salts of the alkyl hydrogen sulfates, for example, the non-polar end is the long chain, and the polar end is the $-OSO_3^- Na^+$ grouping.

These detergents act in essentially the same way as soap does. They are used because they have certain advantages. For example, sodium alkyl sulfates retain their efficiency in hard water, since the corresponding calcium and magnesium salts are soluble. Being salts of strong acids, the sodium alkyl sulfates yield neutral solutions, in contrast to the soaps, which, being salts of weak acids, yield slightly alkaline solutions (Sec. 16.10).

17.27 Unsaturated fats. Hardening of oils. Drying oils

We can see in Table 17.3 that fats contain, in varying proportions, glycerides of certain unsaturated carboxylic acids. The most common of these acids are:



Other things being equal, unsaturation in a fat tends to lower its melting point and thus tends to make it a liquid at room temperature. In the

United States the long established use of lard and butter for cooking purposes has led to a prejudice against the use of the cheaper, equally nutritious oils. Hydrogenation of some of the double bonds in such cheap fats as cottonseed oil, corn oil, and soy bean oil converts these liquids into solids having a consistency comparable to that of lard or butter. This *hardening* of oils is the basis of an important industry that produces cooking fats (e.g., Crisco, Spry) and oleomargarine. Hydrogenation of the carbon-carbon double bonds takes place under such mild conditions (Ni catalyst, 175-190°, 20-40 lb/in.²) that hydrogenolysis of the ester linkage does not occur.

Hydrogenation not only changes the physical properties of a fat, but also — and this is even more important — changes the chemical properties: a hydrogenated fat becomes *rancid* much less readily than does a non-hydrogenated fat. Rancidity is due to the presence of volatile, bad-smelling acids and aldehydes. These compounds result (in part, at least) from attack by oxygen at reactive allylic positions in the fat molecules; hydrogenation slows down the development of rancidity presumably by decreasing the number of double bonds and hence the number of allylic positions.

Linseed oil and tung oil have special importance because of their high content of glycerides derived from acids that contain two or three double bonds. They are known as *drying oils* and are important constituents of paints and varnishes. The “drying” of paint does not involve merely evaporation of a solvent (turpentine, etc.), but rather a chemical reaction in which a tough organic film is formed. Aside from the color due to the pigments present, protection of a surface by this film is the chief purpose of paint. The film is formed by a polymerization of the unsaturated oils that is brought about by oxygen. The polymerization process and the structure of the polymer are extremely complicated and are not well understood. The process seems to involve, in part, free radical attack at reactive allylic hydrogens, free radical addition polymerization similar to that previously described (Sec. 6.20), and cross-linking by oxygen analogous to that by sulfur in vulcanized rubber (Sec. 6.21).

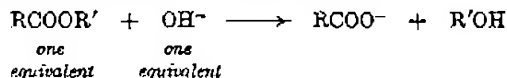
17.28 Analysis of carboxylic acid derivatives. Saponification equivalent

Functional derivatives of carboxylic acids are recognized by their hydrolysis — under more or less vigorous conditions — to carboxylic acids. Just *which kind* of derivative it is is indicated by the other products of the hydrolysis.

Problem 17.7 Which kind (or kinds) of acid derivative is indicated by the following products of hydrolysis?

tained is also identified (Sec. 12.11). (In the case of a substituted amide, Sec. 20.7, the amine obtained is identified, Sec. 20.14.)

If an ester is hydrolyzed in a known amount of base (taken in excess), the amount of base used up can be measured and used to give the saponification equivalent: the equivalent weight of the ester, which is similar to the neutralization equivalent of an acid (see Sec. 16.22).



Problem 17.8 (a) What is the saponification equivalent of *n*-propyl acetate? (b) There are eight other simple aliphatic esters that have the same saponification equivalent. What are they? (c) In contrast, how many simple aliphatic acids have this equivalent weight? (d) Is saponification equivalent as helpful in identification as neutralization equivalent?

Problem 17.9 (a) How many equivalents of base would be used up by one mole of methyl phthalate, $\text{o-C}_6\text{H}_4(\text{COOCH}_3)_2$? What is the saponification equivalent of methyl phthalate? (b) What is the relation between saponification equivalent and the number of ester groups per molecule? (c) What is the saponification equivalent of glyceryl stearate (tristearin)?

PROBLEMS

1. Draw structures and give names of:

- nine isomeric esters of formula $\text{C}_8\text{H}_{16}\text{O}_2$
- six isomeric esters of formula $\text{C}_8\text{H}_{14}\text{O}_2$
- eleven isomeric esters of formula $\text{C}_{14}\text{H}_{28}\text{O}_2$ (Hint: three of these are methyl esters.)

2. Write balanced equations, naming all organic products, for the reaction (if any) of *n*-butyl chloride with:

- | | |
|-----------------------------------|---|
| (a) H_2O | (h) alcoholic AgNO_3 |
| (b) isopropyl alcohol | (i) CH_3NH_2 |
| (c) <i>p</i> -nitrophenol | (j) $(\text{CH}_3)_3\text{NH}$ |
| (d) ammonia | (k) $(\text{CH}_3)_3\text{N}$ |
| (e) toluene, AlCl_3 | (l) $\text{C}_6\text{H}_5\text{NH}_2$ |
| (f) nitrobenzene, AlCl_3 | (m) $(\text{C}_6\text{H}_5)_2\text{Cd}$ |
| (g) NaHCO_3 (aq) | (n) $\text{C}_6\text{H}_5\text{MgBr}$ |

(Check your answers to (i) through (l) in Sec. 20.7.)

3. Answer Problem 2, parts (a) through (l) for acetic anhydride.

4. Write balanced equations, naming all organic products, for the reaction (if any) of phenylacetamide with:

- hot HCl (aq)
- hot NaOH (aq).

5. Answer Problem 4 for phenylacetonitrile.

6. Write balanced equations, naming all organic products, for the reaction (if any) of methyl *n*-butyrate with:

- | | |
|--|--|
| (a) hot H_2SO_4 (aq) | (f) phenylmagnesium bromide |
| (b) hot KOH (aq) | (g) isobutylmagnesium bromide |
| (c) isopropyl alcohol + H_2SO_4 | (h) H_2 , $\text{CuO} \cdot \text{CuCr}_2\text{O}_4$, heat, pressure |
| (d) benzyl alcohol + $\text{C}_6\text{H}_5\text{CH}_2\text{ONa}$ | (i) LiAlH_4 , then acid |
| (e) ammonia | (j) Na , $\text{C}_2\text{H}_5\text{OH}$ |